

METHOD FOR PREPARING SELF-ASSEMBLED SILICON NANOTUBES BY**HYDROTHERMAL METHOD****JAPANESE PCT/PTO 05 MAY 2006****FIELD OF THE INVENTION****CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This Application is a U.S. National Phase of the International Application No. PCT/CN05/000630 filed May 8, 2005 designating the U.S. and published on November 17, 2005 as WO 05/108288, which claims priority to Chinese Patent Application No. 200410023180.1, filed May 11, 2004 and Chinese Patent Application No. 200410063033.7, filed July 6, 2004.

BACKGROUND OF THE INVENTION**Field of the Invention**

[0002] The present invention is related to the-a method for the preparation of self-assembled silicon nanotubes (SiNTs), in particular, to the-a method for the synthesis of self-assembled SiNTs from inorganic solution (hydrothermal solution).

BACKGROUND TECHNOLOGY**Description of the Related Art**

[0003] Although the difficulty for-in the synthesis of SiNTs is widely attributed to the sp³ hybridization in silicon, the possibility of the existence of SiNTs has been suggested theoretically. The preparation of SiNTs, especially self-assembled SiNTs is still very challenging at present. Great interest has focused on carbon nanotubes (CNTs) owing to its~~their~~ excellent properties, which is hot topic worldwide. Many and many researchers in the world are attempting to prepare self-assembled SiNTs. Recently SiNTs were prepared using a template method respectively by Jeong and his coworkers in Sungkyunkwan University, and Sha and his coworkers in Zhejiang University. The corresponding research results were published in Advanced Materials (Adv Mater), which is a famous international journal in the field of materials.

[0004] SiNTs with thean outer diameter of less than 100 nm were synthesized by Jeong and his coworkers using alumina templates. The templates were brought into the-a

molecular beam epitaxy (MBE) chamber where the chamber was evacuated to a pressure of 5×10^{-10} Torr. The Si atoms/clusters were sputtered for 10min by an electron-beam evaporator. The temperature of alumina templates was maintained at 400°C . After the deposition, the sample was further heat treated at 600°C or 750°C under ambient conditions for oxidation.

[0005] SiNTs with thean outer diameter of less than 100 nm were also fabricated by Sha and his coworkers using a nanochannel Al_2O_3 (NCA), silane as the silicon source, and gold as the catalyst in the case of 620□at 620°C and 1450Pa by a chemical vapor deposition (CVD) process.

[0006] Although SiNTs hadhave been prepared by the alumina template and NCA, the SiNTs were formed in the inner wall of templates, by aggregation and not independent on the by self-assembled growth of elementthe elemental Si. Therefore SiNTs obtained by the templates are not the realreally self-assembled SiNTs.

DESCRIPTION OF THE INVENTION

SUMMARY OF THE INVENTION

[0007] The purpose One objective of the invention is to prepare self-assembled SiNTs withfrom silicon source materials without metallic catalysts and templates. The This method takes great has many advantages efincluding simple process, easy to operate and control the equipment, low cost and without the no pollution and is a kind of. In addition, a hydrothermal method may be used to prepare self-assembled SiNTs with small diameter and uniform diameter distribution.

[0008] The preparation of self-assembled SiNTs can be performed by the following process: Water is the solvent. The rate One embodiment provides a method for preparing self-assembled SiNTs comprising forming a mixture of silicon oxide and water is from, wherein the mixture has a silicon oxide to water ratio of 0.01% to 10wt%. The silicon oxide and water are mixed, and then the mixture is put into sealed reaction kettle under the condition of 200–500□, 3–40MPa and is maintained for 1–5h with the equably stirring. % by weight. The mixture is maintained at a temperature of about 200°C to about 500°C and a pressure of about 3 MPa to about 40 MPa for 1 to 5 hours while stirring.

The mixture is stirred using the magnetic stirrer.

~~In preferably, the rate of silicon oxide and solvent is 0.05-8wt%.~~

~~In further preferably, the rate of silicon oxide and solvent is 0.1-6wt%.~~

~~The self assembled SiNTs can be prepared under the preferred conditions of 250-500 $^{\circ}$ of temperature, 8-35MPa of pressure and the temperature and pressure will be maintained for 1-4h with the equably stirring.~~

~~The more preferred preparation conditions in present invention are as follows:~~

~~Temperature: 300-450 $^{\circ}$. Pressure: 10-30MPa. The temperature and pressure will be maintained for 1-3h with the equably stirring.~~

~~The other more preferred preparation conditions in present invention are as follows:~~

~~Temperature: 300-400 $^{\circ}$. Pressure: 6-10MPa. The temperature and pressure will be maintained for 3-4h with the equably stirring.~~

[0009] ~~No metallic catalysts and templates are used in the preparation method disclosed in present invention. The SiNTs prepared by present invention are identified as a kind of self assembled SiNTs according to the results of characterization. The shortages of the common nanoscale materials reuniting easily and dispersing difficultly in the prior art are overcome because the self assembled SiNTs are obtained from the water solution in which no reuniting and intertwist happen.~~ Another embodiment provides a self-assembled silicon nanotube comprising a tubular body having a crystalline silicon wall layer having a thickness of about 5 nm or less and defining an inner pore diameter of about 5 nm or less. The tubular body has an outer amorphous silica layer having a thickness of less than 2 nm. The tubular body has closed ends and an outer diameter in the range of about 8 to 20 nm.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Fig. 1 is a self-assembled growth schematic of the self-assembled SiNTs.

[0011] Fig. 2 is a transmission electron microscopy (TEM) image of the self-assembled SiNTs prepared in accordance with one embodiment of the invention.

[0012] FIG. 3 is a selected area electron diffraction (SAED) image of the self-assembled SiNTs prepared in accordance with one embodiment of the invention.

[0013] FIG. 4 is the energy dispersive X-ray spectroscopy (EDS) of the self-assembled SiNTs prepared in accordance with one embodiment of the invention.

[0014] FIG. 5 is a high-resolution transmission electron microscopy (HRTEM) image of a tubular body of the self-assembled SiNTs prepared in accordance with one embodiment of the invention.

[0015] FIG. 6 is a HRTEM image of a tubular growth tip of the self-assembled SiNTs prepared in accordance with one embodiment of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] The preparation of self-assembled SiNTs can be performed by the following process. Silicon oxide is mixed with water (e.g., a solvent) to form a mixture with a silicon oxide to water ratio of 0.01% to 10% by weight. Once the silicon oxide and water are mixed, the mixture is put into a sealed reaction kettle or container. The reaction container is maintained under the condition of about 200-500°C and about 3-40 MPa of pressure for 1-5 hours with substantially uniform stirring. The mixture may be stirred using a magnetic stirrer. In one embodiment, the ratio of silicon oxide to water is preferably 0.05% to 8% by weight, and more preferably 0.1% to 6% by weight.

[0017] In another embodiment, the self-assembled SiNTs can be prepared under conditions with a temperature of 250°C to 500°C and a pressure of 8 MPa to 35 MPa for 1-4 hours with substantially uniform stirring. In a more preferred embodiment, the self-assembled SiNTs can be prepared under conditions with a temperature of 300°C to 450°C and a pressure of 10 MPa to 30 MPa for 1-3 hours with substantially uniform stirring. In another more preferred embodiment, the self-assembled SiNTs can be prepared under conditions with a temperature of 300°C to 400°C and a pressure of 6 MPa to 10 MPa for 3-4 hours with substantially uniform stirring.

[0018] No metallic catalysts and templates are used in the preparation of SiNTs using the hydrothermal method disclosed in the present invention. The SiNTs prepared by the hydrothermal method of the present invention are identified as a kind of self-assembled SiNTs according to the results of characterization. The common problems of nanoscale materials, including the ease of congregation and the difficulty of dispersion, are solved because the self-assembled SiNTs are obtained from water where no congregation occurs. At the same time, the self-assembled SiNTs makes it possible to increase the strength and toughness of composites, owing due to the ability of forming SiNTs with large rate of larger

length and to diameter ratios. A great deal of research shows that Many researchers have shown that silicon nanowirenanowires (SiNWs) have greatly great potential and for practical applications owing due to its the typical quantum confinement effect and excellent physical properties. However, theoretical research shows Theoretical studies have shown that SiNTs can take advantage of the quantum confinement effect more easily and can be more stable than SiNWs. Therefore, SiNTs are predicted to have the be a promising for the application in nanodevices in the future and become a new nanoscale material for potential applications in the nanotechnology field, which provides a new approach for themaking nanodevices to be that are highly integrated and miniaturized.

[0019] The preparation method of the present invention is simple, operatingoperates simply and easily, and. Since simple equipment is used and, the low cost is low. This preparation creates can provide the opportunity for the practical applications of the self-assembled SiNTs. Innoxious starting materials are used in the invention. The starting materials and preparation the process are all unpolluted to do not pollute the environment absolutely, which accords with the development trend of modern industry for environment protection. Therefore, the, and therefore large quantities of self-assembled SiNTs can be prepared industrially in accordance with the development trend of modern industry for environmental protection.

[0020] The growth mechanism of the self-assembled SiNTs prepared by the method of present invention is simply introduced as the following: Self assembled growth mechanism of SiNTs is proposed preliminarily according tobased on the “lip-lip” interaction growth model proposed by Charlier et al. During the growth phase of the nanotubes, chemical bondings bonding at the end of nanotubes (NTs) is in a metastable energy minimum, which prevents the closure of the growth end of NTs. The atoms of forming nanotubes connect with each other continuously resulting in the sustaining sustained growth of NTs. With the change of conditions, such as the decrease of temperature, the chemical bonding of the growth end of growing NTs is tending toapproaches a more stable state resulting in the closure of the growth end of NTs because. Since the closed structure is more stable than the initial open end structure.state, it results in the closure of the growth end of NTs.

[0021] Fig. 1 is a schematic of the growth process schematic of self-assembled SiNTs. Chemical bondings between atoms are all in a metastable state and abundant H⁺, Si atoms and O²⁻ atoms occur because Si and silicon oxide are in the state of gaseity and react between them also occurs under are formed due to the high temperature and high pressure of the hydrothermal condition, and the reactive nature of the Si and silicon oxide in gaseous form. Nucleation starts relatively equally uniformly from the vapor substances in the reaction kettle owing to because of the equally stirring of magnetic stirrer in the preparation process. Then the temperature risingrises rapidly in the kettle shows that much heat is given out demonstrating due to the exothermic process, which suggests that the growth process of the SiNTs has taken place. There is a temperature fieldgradient inside the reaction container, i.e. the temperature gradsgoes from high temperature area in the center of the reaction kettle to low temperature area in at the edge of the reaction kettle. The tubular structures are elementarilyinitially formed in the low temperature area due to combining where the Si and Si connect during the growth of SiNTs (Fig. 1(a)). The Si-Si bonding inat the growth edge of the tubular structures in a metastable energy minimum prevents the closure of the growth edge of SiNTs. At the same time, the possibility of collision opportunity with different atoms increases because SiNTs move continually between low temperature areaareas and high temperature areaareas with the stirring of stirrer. Thus abundant Si atoms in high temperature areaareas enter into the tubular walls of SiNTs and are combined with Si of in the tubular wall resulting in the one-dimensional growth of SiNTs along the temperature field direction. The gradient.

[0022] A stable SiO₂ layers form by the reaction of layer is formed when the Si atoms inat the interface of the tube wall and atoms the atomic O²⁻ in the environment react with each other, therefore preventing the growth of SiNTs in non-one-dimensional direction (Fig. 1(b)). Because a Abundant H⁺ exists in the hydrothermal condition, thus may cause one of four Si atoms in the crystalline Si is to be substituted by H⁺ and possibly cause a part of crystalline Si in the tubular wall of SiNTs is possible to become amorphous Si resulting in the . The possible result is the formation of crystalline Si layers with a tubular wall that is similar to a graphite layer structure.

[0023] Once the heating of the reaction kettle has been stopped, Si-Si-Si bondings in bonding at the growth end of SiNTs is changing changed gradually from the metastable state to the more stable state gradually due to the falling of temperature and pressure after heating is stopped. Simultaneously, At the same time, the temperature gradient in the kettle also disappears gradually slowly disappears, resulting in the closure of the growth end and the growth of SiNTs stops (-Fig. 1(c), (d)).

BRIEF DESCRIPTIONS OF THE DRAWINGS

Fig. 1 is the self assembled growth schematic of the self assembled SiNTs.

Fig. 2 is the transmission electron microscopy (TEM) image of the self assembled SiNTs prepared in the invention.

Fig. 3 is the selected area electron diffraction (SAED) image of the self assembled SiNTs prepared in the invention.

Fig. 4 is the energy dispersive X ray spectroscopy (EDS) of the self assembled SiNTs prepared in the invention.

Fig. 5 is the high resolution transmission electron microscopy (HRTEM) image of tubular body of the self assembled SiNTs prepared in the invention.

Fig. 6 is the HRTEM image of tubular growth tip of the self assembled SiNTs prepared in the invention.

[0024] The TEM image of the self-assembled SiNTs in Fig. 2 shows that abundant nanotubes are visible in the figure were formed using the hydrothermal method. Most nanotubes are straight in shape and the surfaces of self-assembled SiNTs are smooth. The outer diameter is common usually less than 5 nm, the distribution range is 8-20 nm about 8-20 nm, and the lengths of SiNTs are several hundreds of nanometers, up to microns. The diameter of the inner pore (e.g., inner diameter) is smaller than 5 nm in general with a small diameter distribution range. The growth tips of the self-assembled SiNTs are in closed semicircular form showing that no catalyst particles exist in the SiNTs and no growth tips with open end structure are observed.

[0025] The self-assembled SiNTs is a kind of are mostly poly-crystalline structure structures according to the SAED pattern (Fig. 3) of the self assembled SiNTs. In that pattern,

the. The SAED patterns of the first, second, and third order diffraction rings respectively, from the inside to the outside of a nanotube, match well with the (1 1 1), (2 2 0) and (3 1 1) diffraction crystal planes, respectively.

[0026] The EDS analysis in Fig. 4 shows that the chemical composition of the products only consists of Si and O and the. The equal peak height of Si and O is same. The suggests that the atomic ratio of Si and O is 1:1, which accordsis consistent with that of silicon monoxide.

[0027] The interplanar spacing, outer diameter and the diameter of inner pore, the thickness of amorphous outer layer and Si wall layer of the inner diameters, the thicknesses of amorphous outer layer and Si wall layer of SiNTs were measured according to the HRTEM measurement and following calculation by the and calculated using a software of by Digital Micrograph applied in the HRTEM. The hollow inner pore, crystalline silicon wall layer and amorphous silica outer layer can be clearly observed obviously fromin the HRTEM images. The crystalline layer grows along the axial direction of SiNTs. The interplanar spacing of crystalline in the SiNTs is around 0.31 nm according to the measurement and the calculation matching well, which agrees with the {111} plane of silicon. The outer diameter of the tubular body in Fig. 5 is about 14 nm, the diameter of inner pore is about 5 nm and the thicknesses of crystalline Si and amorphous outer layer are about 5 nm and less than 2 nm, respectively. The outer diameter of the tubular growth tip in Fig. 6 is about 18 nm and the diameter of inner pore is about 3 nm which. The inner diameter of the growth tip is larger than that of the tubular body. The corresponding thickness of Si wall thickness is 5 nm and the amorphous outer layer thickness less than 2 nm.

[0028] The amorphous silicon oxide outer layer in at the growth tip of the self-assembled SiNTs distributes asymmetrically does not distribute evenly and some defects exist in the SiNTs. The amorphous outer layers can be identified to be amorphous silica oxide because the environment in the reaction kettle is a kind of oxidation environment, only silicon and oxygen exist in the sample and silica oxide is the most stable compound silica. The environment in the reaction kettle is an oxidation environment, and there are two elements Si and O in the products (e.g., SiNTs). Since silicon oxide is the most stable compound of silica, the outer layers of the SiNTs can be identified as amorphous silica. The appearance of

the same number of lattice fringes and amorphous silica outer layers from both sides of the self-assembled SiNTs shows that it has a seamless tubular structure. Therefore, the structures of SiNTs are composed of three parts: hollow inner pore with a diameter of several nanometers in the middle, crystalline silicon wall layers with a thickness of less than 5 nm and amorphous silica outer layers with less than 2 nm thickness.

EMBODIMENTS

Example 1

[0029] 1. Silicon oxide and water with a rate of 0.01 wt% were mixed together to form a mixture of 0.01% by weight, and then put into the mixture was place in a sealed reaction kettle. The mixture was maintained at 200°C under 3 MPa pressure for 1 hour with substantially uniform stirring using a magnetic stirrer. Self-assembled SiNTs with the an average inner diameter of inner pore of less than 5 nm and around 15nm in the an average outer diameter of around 15 nm were prepared under the conditions of 200° of temperature, 3MPa of pressure and the temperature and pressure are maintained for 1h with the equally stirring of magnetic stirrer formed.

Example 2

[0030] 2. Silicon oxide and water with a rate of 0.1wt% were mixed together to form a mixture of 0.1% by weight, and then put into the mixture was place in a sealed reaction kettle. The mixture was maintained at 380°C under 8 MPa pressure for 1 hour with substantially uniform stirring using a magnetic stirrer. Self-assembled SiNTs with the an average inner diameter of inner pore of less than 5 nm and around 15nm in the an average outer diameter of around 15 nm were prepared under the conditions of 380° of temperature, 8MPa of pressure and the temperature and pressure are maintained for 1h with the equally stirring of magnetic stirrer formed.

Example 3

[0031] 3. Silicon oxide and water with a rate of 0.5wt% were mixed and then put together to form a mixture of 0.5% by weight, and the mixture was place in a sealed reaction kettle. The mixture was maintained at 500°C under 8 MPa pressure for 1 hour with substantially uniform stirring using a magnetic stirrer. Self-assembled SiNTs with the an

average inner diameter of inner pore of less than 5 nm and around 15nm in the an average outer diameter of around 15 nm were prepared under the conditions of 500 \square of temperature, 8 MPa of pressure and the temperature and pressure are maintained for 1h with the equably stirring of magnetic stirrer formed.

Example 4

[0032] 4. Silicon oxide and water with a rate of 1wt% were mixed and then put into together to form a mixture of 1% by weight, and the mixture was place in a sealed reaction kettle. The mixture was maintained at 300°C under 10 MPa pressure for 3 hours with substantially uniform stirring using a magnetic stirrer. Self-assembled SiNTs with the an average inner diameter of inner pore of less than 5 nm and around 15nm in the an average outer diameter of around 15 nm were prepared under the conditions of 300 \square of temperature, 10 MPa of pressure and the temperature and pressure are maintained for 3h with the equably stirring of magnetic stirrer formed.

Example 5

[0033] 5. Silicon oxide and water with a rate of 4wt% were mixed together to form a mixture of 4% by weight, and then put into the mixture was place in a sealed reaction kettle. The mixture was maintained at 380°C under 15 MPa pressure for 1 hour with substantially uniform stirring using a magnetic stirrer. Self-assembled SiNTs with the an average inner diameter of inner pore of less than 5 nm and an average outer diameter of around 15 nm in the average outer diameter were prepared under the conditions of 380 \square of temperature, 15 MPa of pressure and the temperature and pressure are maintained for 1h with the equably stirring of magnetic stirrer formed.

Example 6

[0034] 6. Silicon oxide and water with a rate of 6wt% were mixed together to form a mixture of 6% by weight, and then put into the mixture was place in a sealed reaction kettle. The mixture was maintained at 500°C under 20 MPa pressure for 1 hour with substantially uniform stirring using a magnetic stirrer. Self-assembled SiNTs with the an average inner diameter of inner pore of less than 5 nm and around 15nm in the an average outer diameter of around 15 nm were prepared under the conditions of 500 \square of temperature,

~~20MPa of pressure and the temperature and pressure are maintained for 1h with the equably stirring of magnetic stirrer-formed.~~

Example 7

[0035] ~~7. Silicon oxide and water with a rate of 6wt% were mixed and then put intotgether to form a mixture of 6% by weight, and the mixture was place in a sealed reaction kettle. The mixture was maintained at 380°C under 8 MPa pressure for 3 hours with substantially uniform stirring using a magnetic stirrer. Self-assembled SiNTs with thean average inner diameter of inner pore of less than 5 nm and around 15nm in thean average outer diameter of around 15 nm were prepared under the conditions of 380□ of temperature, 8MPa of pressure and the temperature and pressure are maintained for 3h with the equably stirring of magnetic stirrer-formed.~~

Example 8

[0036] ~~8. Silicon oxide and water with a rate of 8wt% were mixed and then put intotgether to form a mixture of 8% by weight, and the mixture was place in a sealed reaction kettle. The mixture was maintained at 500°C under 30 MPa pressure for 2 hours with substantially uniform stirring using a magnetic stirrer. Self-assembled SiNTs with thean average inner diameter of inner pore of less than 5 nm and around 15nm in thean average outer diameter of around 15 nm were prepared under the conditions of 500□ of temperature, 30MPa of pressure and the temperature and pressure are maintained for 2h with the equably stirring of magnetic stirrer-formed.~~

Example 9

[0037] ~~9. Silicon oxide and water with a rate of 10wt% were mixed and then put intotgether to form a mixture of 10% by weight, and the mixture was place in a sealed reaction kettle. The mixture was maintained at 500°C under 30 MPa pressure for 4 hours with substantially uniform stirring using a magnetic stirrer. Self-assembled SiNTs with thean average inner diameter of inner pore of less than 5 nm and around 15nm in thean average outer diameter of around 15 nm were prepared under the conditions of 500□ of temperature, 30MPa of pressure and the temperature and pressure are maintained for 4h with the equably stirring of magnetic stirrer-formed.~~

Example 10

[0038] 40. Silicon oxide and water ~~with a rate of 8wt%~~ were mixed together to form a mixture of 8% by weight, and then put into the mixture was place in a sealed reaction kettle. The mixture was maintained at 450°C under 30 MPa pressure for 3 hours with substantially uniform stirring using a magnetic stirrer. Self-assembled SiNTs with thean average inner diameter of inner pore of less than 5 nm and around 15nm in thean average outer diameter of around 15 nm were prepared under the conditions of 450°C of temperature, 30MPa of pressure and the temperature and pressure are maintained for 3h with the equably stirring of magnetic stirrer. formed.

We claim

1. The method for preparing self assembled SiNTs by hydrothermal method, characterized in that: water is the solvent; the rate of silicon oxide and solvent is 0.01-10wt%; the silicon oxide and water are mixed and then put into the sealed reaction kettle; the preparation parameters are 200-500 \square of temperature, 3-40MPa of pressure, and the temperature and pressure are maintained 1-5h with the equably stirring.
2. The method for preparing self assembled SiNTs by hydrothermal method according to claim 1, characterized in that the stirring is performed using the magnetic stirrer.
3. The method for preparing self assembled SiNTs by hydrothermal method according to claim 1, characterized in that the rate of silicon oxide and solvent is 0.05-8wt%.
4. The method for preparing self assembled SiNTs by hydrothermal method: The according to claim 1, characterized in that the rate of silicon oxide and solvent is 0.1-6wt%.
5. The method for preparing self assembled SiNTs by hydrothermal method according to one of claim 1 to 4, characterized in that the preparation parameters are 250-500 \square of temperature, 8-35MPa of pressure and the temperature and pressure are maintained 1-4h with the equably stirring.
6. The method for preparing self assembled SiNTs by hydrothermal method preparation parameters are 300-450 \square of temperature, 10-30MPa of pressure and the temperature and pressure are maintained 1-3h with the equably stirring.
7. The method for preparing self assembled SiNTs by hydrothermal method according to one of claim 1 to 4, characterized in that the preparation parameters are 300-400 \square of temperature, 6-10MPa of pressure and the temperature and pressure are maintained 2-4h with the equably stirring.

ABSTRACT

The present invention relates to a method for preparing self-assembled silicon nano-tube by hydrothermal method. In the method, water is used as solvent, and non-toxic silicon oxide is added to the water, then mixture of the water and silicon oxide is fed into a sealed reaction kettle while stirring, the mixture is kept at a certain temperature and a certain pressure for a period of time; the weight of the said silicon oxide is not more than 10% of weight of the solvent, and a magnetic stirrer is used for stirring. The present invention completely utilizes non-toxic raw materials, and the materials and preparation process do not pollute the environment, so the method satisfies the development trend of modern industry.

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